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学位論文内容の要旨

博士の専攻分野の名称　博士（理学）　氏名　Liu　Ran

学位論文題名

High-Pressure Synthesis, Crystal Structures and Physical Properties of A-Site Columnar-Ordered Quadruple Perovskites
（A サイト柱状秩序型四重ペロブスカイトの高圧合成と結晶構造と物性）

Perovskite material is very popular in inorganic and solid-state chemistry areas for decades. Depending on the correlated phenomena involving spin, charge, and orbital degrees of freedom of unpaired electrons, the crystal structure, physical and chemical properties -thermoelectric, electrochemical, catalytic, and multiferroic- are complex but attractive. The general chemical formula of perovskite is ABO_3, such as $CaTiO_3$, while more complicated compositions like $A'A_3B_4O_{12}$ and $A_2A'A''B_4O_{12}$ are also reported for many perovskites. This study has used rare earth, transition metal, and alkaline metal oxides to create new perovskite-based materials. The crystal structures, magnetic properties, and physical properties have been investigated.

Chapter 1 introduces the general background including the structure, magnetism, and application.

Chapter 2 presents the outline of experimental techniques used in this study.

Chapter 3 introduces the perovskite $Y_2MnGa(Mn_{4-x}Ga_x)O_{12}$ synthesized at high pressure and high-temperature conditions. Synchrotron X-ray and neutron powder diffraction were used to study the crystal structures and cation distributions. The solutions adopt the structure type of the A-site columnar-ordered quadruple perovskite family with the space group of $P4_2/nmc$. The x = 0 compound has a cation distribution of $[Y_2^{3+}]_A[Mn^{3+}]_{A'}[Ga^{3+}_{0.68}Mn^{2+}_{0.32}]_{A''}[Mn_{3.68}Ga_{0.32}]_BO_{12}$ with a preferred localization of Ga^{3+} in the tetrahedral A" site and with a small amount of Ga^{3+} in the octahedral B site. A complete triple A-site order, $[Y_2^{3+}]_A[Mn^{3+}]_{A'}[Ga^{3+}]_{A''}[Mn^{3+}_{4-x}Ga_{3+x}]BO_{12}$, is realized for x ≧ 1. All samples demonstrated spin-glass-like magnetic properties at low temperatures. First-principles calculations indicated the spin-glass-like magnetic ordering is derived from the Ga substitution to the B sites and gave evidence that the ideal cation distribution could produce robust ferromagnetism in this family of perovskites.

Chapter 4 presents $R_2MnMn(MnTi_3)O_{12}$ oxides, belonging to a family of A-site columnar-ordered quadruple perovskites. They were synthesized by a high-pressure and high-temperature method for R = Nd, Eu, and Gd at about 6 GPa and 1570 K. At room temperature they crystallize in centrosymmetric space group $P4_2/nmc$, and their crystal structures were studied by synchrotron powder X-ray diffraction. They exhibit broad dielectric anomalies below room temperature with characteristic frequency-dependent features of the relaxor ferroelectric behavior. $P-E$ loop measurements at 77 K confirmed ferroelectricity for R = Nd and Eu. Magnetic and specific heat measurements showed the presence of long-range ferrimagnetic transitions below 20 K (R = Nd), 30 K (R = Eu), and 42 K (R = Gd). Additional specific heat anomalies were observed below about 5 K for R = Nd and Gd probably due to the involvement of rare-earth cations in long-range orderings. The coexistence of ferrimagnetic transitions and relaxor-like ferroelectric properties make $R_2MnMn(MnTi_3)O_{12}$ perovskites multiferroic materials.

Chapter 5 introduces $NaRMn_2Ti_4O_{12}$ compounds (R = Sm, Eu, Gd, Dy, Ho, and Y) synthesized under high pressure (about 6 GPa) and high temperature (about 1750 K) conditions. The compounds adopt an A-site columnar-ordered quadruple-perovskite structure with the generic chemical formula $A_2A'A''B_4O_{12}$. Their crystal structures were studied by powder synchrotron X-ray and neutron diffraction at temperatures between 1.5 and 300 K. Those maintain a paraelectric structure with centrosymmetric space group $P4_2/nmc$ at all temperatures, in comparison with the related $CaMnTi_2O_6$ perovskite, in which a ferroelectric transition occurs at 630 K. The centrosymmetric structure was also confirmed by second-harmonic generation. It has a cation distribution of $[Na^+R^{3+}]_A[Mn^{2+}]_{A'}[Mn^{2+}]_{A''}[Ti_4^{4+}]_BO_{12}$ (to match with the generic chemical formula) with statistical distributions of Na^+ and R^{3+} at the large A site and a strongly split position of Mn^{2+} at the square-planar A' site. We found a C-type long-range antiferromagnetic structure of Mn^{2+} ions at the A' and A" sites below $T_N = 12$ K for R = Dy. All compounds show large dielectric constants of a possible extrinsic origin similar to that of $CaCu_3Ti_4O_{12}$. $NaRMn_2Ti_4O_{12}$ with R = Er–Lu crystallized in the $GdFeO_3$-type $Pnma$ perovskite structure, and $NaRMn_2Ti_4O_{12}$ with R = La, Nd contained two perovskite phases: an $AA'_3B_4O_{12}$-type $Im\overline{3}$ phase and a $GdFeO_3$-type $Pnma$ phase.

Chapter 6 presents the general conclusion and future prospects based on this study.